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淀粉和葡萄糖化学转化为果糖的研究

Study on the Conversion of Starch and Glucose into Fructose

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摘　要

在全球经济和工业高速发展的同时，化石能源日渐减少，环境污染和生态恶化等问题日益严重，因此寻找可再生资源以缓解当前的能源和环境危机迫在眉睫。生物质资源被认为唯一能替代化石能源以获取高附加值化学品、生物燃料和能源材料的绿色、可再生资源。碳水化合物是生物质资源中储量最丰富的组分，而淀粉是人类饮食中最为丰富的碳水化合物，将其转化为果糖是当前开发利用生物质资源的研究热点。果糖作为生物质重要的衍生化学品之一，是一种重要的食品甜味剂和制备生物基化学品最为活跃的原材料，市场上对果糖的需求不断扩大，其在燃料和能源材料等方面的应用也逐渐被挖掘出来。碳水化合物先水解为葡萄糖而后葡萄糖通过异构化反应转化为果糖，葡萄糖异构化为果糖是碳水化合物转化为平台化学品和生物燃料关键的中间步骤。本论文以绿色化学为宗旨，以淀粉和葡萄糖为原料，针对目前葡萄糖异构化反应中存在的问题展开了一系列研究，包括绿色环保、价格低廉和制备简单的催化剂的开发，各步反应条件的优化以及5-羟甲基糠醛（HMF）制备体系的建立等，并取得了一定的研究成果。

首先，在水体系中，以硫酸湿法浸渍沸石分子筛得到一类新型负载催化剂，能催化淀粉一锅法制备果糖，发现固体酸催化剂SO42-/USY表现出良好的催化活性，果糖的得率最高。各种反应条件对果糖的得率都具有较大的影响，在5 wt.%淀粉（淀粉/水）、催化剂用量为淀粉质量的30 wt.%、反应温度为150 oC、反应时间为1 h、转速为400 rpm的条件下，能得到得率最高的果葡糖浆，含27.84%的果糖和58.34%的葡萄糖。通过对催化剂进行物理吸附表征，发现USY具有较高的孔隙度和比表面积，通过浸渍焙烧过程能有效使SO42-与USY通过键合作用吸附在USY表面上。同时催化剂在使用过程中表现出重复使用性能不佳的缺点，通过对催化剂进行化学吸附和元素分析表征，发现催化剂活性的降低与含碳有机质沉积和SO42-催化活性中心的流失有关。在此基础上开发了一套通过简单的焙烧（除去表面积碳）和硫酸中浸渍活化（增加SO42-）的催化剂再生方法，可以有效地恢复SO42-/USY的催化活性。

其次，建立了淀粉两步法制备果糖的高效反应路线。第一步是用超低酸水解淀粉制

备葡萄糖，第二步是用碱性催化剂催化葡萄糖异构化为果糖。第一步当淀粉浓度为5 wt.%，硫酸浓度为8 mM，在150 oC反应1 h，能获得103.83%的葡萄糖得率，淀粉几乎完全水解为葡萄糖。第二步选取实验室常见的碱性催化剂作为考察对象，发现一系列强碱弱酸盐和有机碱对葡萄糖异构化反应均具有良好的催化效果。在强碱弱酸盐中选用安全无毒并且易于去除的碳酸钠为催化剂，当葡萄糖浓度为5 wt.%（葡萄糖/水），碳酸钠用量为35 wt.%（碳酸钠/葡萄糖），在65 oC反应3 h，葡萄糖转化率为62.37%，果糖选择性为64.34%，果糖得率为40.13%。在有机碱中选用可作为营养品添加剂的胆碱为催化剂，当葡萄糖浓度为5 wt.%（葡萄糖/水），胆碱用量为10 wt.%（胆碱/葡萄糖），在65 oC反应3 h，葡萄糖转化率为53.25%，果糖选择性为80.38%，果糖得率为42.8%。同时，研究发现：葡萄糖的异构化反应与催化剂的种类无关，而与反应体系pH值有很大相关性。只要在合适的pH值范围就可以得到高得率的果糖。

然后，在以胆碱为催化剂的基础上添加一定量的硼砂能够进一步提高葡萄糖异构化效率，证明硼砂具有良好的助催化作用。另外，根据硼砂的特性，提出了硼砂助催化葡萄糖异构化制备果糖的可能反应机理。

最后，在以上实验研究的基础上，建立了葡萄糖两步制备HMF的温和、高效的反应路线。第一步用胆碱和硼砂协同催化葡萄糖异构化为果糖；第二步将生成的果糖与氯化胆碱形成低共熔溶剂制备HMF。其中，在氯化胆碱4倍量wt/wt（氯化胆碱/生成的果糖）、1 wt.%盐酸（盐酸/果糖）、100 oC反应4 h的条件下，能获得70.8 mol%的HMF得率。胆碱和氯化胆碱催化体系与目前报道的氯化铬离子液体催化体系相比，避免了有毒铬离子催化剂污染环境的问题且具有方法简单、条件温和、价格低廉、绿色环保等优点，为今后HMF的规模化生产提供了一定的理论指导和可行措施。

关键词：淀粉；固体酸；葡萄糖；异构化；果糖；碱；硼砂；p； HMF

Abstract

With the fast development of world economy, the diminishment of fossil resources and the gradual deterioration of global ecological environment, finding renewable resources to alleviate the current energy and environmental crisis is imminent. Biomass is considered to be the only renewable resources in nature to replace the fossil fuels for the production of high value added chemicals, biofuels and energy materials. The conversion of carbohydrates, which are the most abundant components of biomass, into fructose is one of the most important ways for the utilization of biomass energy. As fructose is an important derivative of biomass, an important sweetener and active raw material for the production of biologic-chemistry matter, its application in food, fuels and energy materials has been gradually excavated. Starch, which is the most abundant component of carbohydrates, can be hydrolyzed to glucose and glucose can be converted to fructose by isomerization. The isomerization of glucose into fructose is considered to be a critical intermediate step in the efficient conversion of renewable lignocellulosic materials into biofuels and platform chemicals. According to the current research progress and existing problems in the isomerization of glucose into fructose, a series of studies on the concept of green chemistry have been carried out in this dissertation. Various low-budget, environmentally friendly, easily prepared catalysts were prepared for the conversion of starch and glucose into fructose, the basic reaction conditions of every step were optimized and the reaction system for the preparation of HMF was established.

Firstly, supporting sulfuric acid on zeolite was found to be an efficient catalyst to bring about the conversion of starch directly into fructose in a one-step reaction. The catalytic efficiency of a series of modified zeolite catalysts for the conversion of starch into fructose was investigated in datails. Among these catalysts used, the SO42-/USY catalyst possessed a bifunction with high activity for both

hydrolysis of starch and isomerization of glucose, which enable one-step preparation of HFCS from starch to turn into reality. An optimized fructose yield of 27.84% was obtained from starch under the following reaction conditions: 5 wt.% starch in water, 30 wt.% SO42-/USY (SO42-/USY /starch), 150 oC, 1 h, 400 rpm. The USY catalyst was found has high specific surface area and porosity characterized by physical adsorption technique, which enable the sulfuric acid to be effectively adsorbed on the USY surface by means of impregnation and calcination. Meanwhile, the catalysts were characterized by NH3-TPD analysis and elemental analysis to find that the decrease of catalytic activity resulted from carbon deposition on the catalysts and the loss of SO42-. Therefore, the catalytic activity of SO42-/USY can be effectively recovered by calcining (removal carbon on the surface of catalyst) and impregnating in sulfuric acid (increase SO42-). Secondly, a high efficient reaction route for the two-step preparation of fructose from starch was established. Step 1, the starch was hydrolyzed into glucose by ultra low acid; step 2, the glucose was isomerized to fructose by basic catalyst. In the first step, the glucose yield of 103.83% (starch was almost completely hydrolyzed to glucose) was obtained under the optimal reaction conditions: 5 wt.% starch in water, 8mM sulfuric acid concentration, 150 oC, 1 h. In the second step, a series of alkali salt and organic alkali were found to have good catalytic efficiency for the isomerization of glucose. Among alkali salt, sodium carbonate was selected as the best catalyst because of the obvious advantages of safety, innocuity and easy to removal. A glucose conversion of 62.37%, a fructose selectivity of 64.34% and a fructose yield of 40.13% were obtained under the following reaction conditions: 5 wt.% glucose in water, 35 wt.% Na2CO3 (Na2CO3/glucose), 65 oC,3 h. Among organic alkali, choline was chosen as the optimal catalyst because it can be used as a nutritional additive. A glucose conversion of 53.25%, a fructose selectivity of 80.38% and a fructose yield of 42.8% were obtained under the following reaction conditions: 5 wt.% glucose in

water, 10 wt.% choline (choline/glucose), 65 oC,3 h. Meanwhile, the study found that with proper pH value, almost all of inorganic bases, organic bases and alkali salt could efficiently isomerize glucose into fructose. The results indicated that the isomerization process was significantly affected by the basicity of reaction system, while the types of alkalines had little effect.

Subsequently, borax could enhance the catalytic efficiency of glucose isomerization by choline. According to the characteristics of borax, the possible reaction mechanism for borax promoting effects on the glucose isomerization was presented.

Eventually, according to the study aforementioned, a mild and high efficient reaction route for the two-step preparation of HMF from glucose was designed and implemented. Step 1, the glucose was isomerized to fructose by choline and borax; step 2, the fructose was converted to HMF with hydrochloric acid induced by choline chloride. An optimized HMF yield of 70.8 mol% was obtained from glucose under the following reaction conditions: 4 wt/wt ChCl (ChCl/fructose), 1 wt.% HCl (HCl/fructose), 100 oC, 4 h. Compared with the preparation of HMF from glucose in metal chloride/ionic liquid reaction system, this reaction system possesses the characteristics of easy process, low investment and benign to environment. This study was drafted to provide a theoretical basis and technical support for the mass production of HMF in the future.

Keywords: starch; solid acid; glucose; isomerization; fructose; base; choline; pH; HMF

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